

THE PREDICTION OF PSEUDO-RESONANCE POSITIONS IN THE SCHWINGER VARIATIONAL PRINCIPLE

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ABSTRACT

The Schwinger Variational Principle is applied to s-wave electron-hydrogen atom scattering. We show computationally, that, consistent with a recent paper by B. Apagyi, P. Levay, and K. Ladanyi², there are pseudo-resonances at the static exchange level of approximation, but not at the static level. We employed the T-matrix as well as the K-matrix version of the Schwinger Principle, with a real Slater basis, and obtained the same results in both. We are able to identify the origin of the pseudo-resonances as resulting from singularities in the separable potential that is effectively employed in the Lippman-Schwinger equation from which the Schwinger Variational Principle can be derived. The determination of the pseudo-resonance parameters from the separable potential is computationally inexpensive and may be used to predict the pseudo-resonance parameters for the scattering calculations so that they may be avoided.

it is shown

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was employed

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Rationale

The present work is a computational study of electron scattering from atomic hydrogen in its ground electronic state. We are studying this system using the Schwinger Variational Principle (SVP). This system has been studied many times before at a very high level of accuracy.¹ It is not our intent to study $e^- + H$ just for the cross section data that result, but rather to study this system as a model system to explore some of the subtle aspects of the SVP. We are primarily interested in electron-molecule collisions where L^2 basis set methods, such as the SVP, have shown the greatest utility, especially for processes such as electronic excitation and dissociative recombination.

However, there are a number of problems that are encountered in using the SVP. In particular, two recent papers^{2,3} have shown that, contrary to the prevalent belief⁴, the SVP does encounter pseudo-resonances, even in the simple s-wave $e^- + H$ system, so long as the exchange effect is included. Indeed, it is necessary to have an energy dependent potential in order to see these pseudo-resonances. At the static level, the pseudo-resonances are not encountered in the SVP, in contrast to the Kohn Variational Principle⁵ (KVP) where they are encountered even at the static level.

This fact apparently led many researchers^{4,6} to conclude that the SVP did not suffer from the occurrence of pseudo-resonances. The argument that was used to explain the assumed non-occurrence of pseudo-resonances in the SVP is based on the paper of Adhikari and Sloan⁷ who show that the derivation of the SVP, from the Lippman-Schwinger equation by taking the variations of the wavefunction and deleting second order terms, is equivalent to approximating the exact potential in the Lippman-Schwinger equation, by the projection of the exact potential onto an L^2 basis set, thus producing a finite rank separable approximation to the exact potential. It was then argued that the SVP implementation was equivalent to solving the Lippman-Schwinger equation exactly for a certain separable potential, and since the solution was exact, no spurious resonances would occur in the solution. This, as it turned out, was true, but a somewhat subtle flaw in the argument leads to pseudo-resonances anyway. We shall presently elaborate.

These false resonances are non-physical. This is especially troubling since resonance processes have turned out to be the predominant mechanism by which molecules are excited and by which molecules dissociate upon scattering by electrons. It is, therefore, extremely important to distinguish the real resonances from the pseudo resonances.

Thus, in order to study the origin and characteristics of these resonances, it is fortuitous to encounter them in so simple a system as s-wave $e^- + H$, at the static exchange level² (static + exchange potential). We therefore decided not only to repeat the calculation of Ref. 2, but also to perform the calculation using the T-matrix approach, as well as the K-matrix approach, in contrast to the authors of Ref. 2 and 3. In doing so, several interesting aspects of the use of the SVP were studied and the origin of the pseudo resonances was explained.

Sketch Of The Theory

The theory for the K-matrix version of the calculation is given rather completely in Ref. 1. We shall just limit our description of the theory to certain fundamental points that are useful to define the differences in our work from Ref. 1 and to facilitate the explanation of our conclusions. We are solving the time-independent Shrödinger equation, for electron-H atom scattering, which, in atomic units, is

$$H\Psi(\vec{r}_1, \vec{r}_2) = E\Psi(\vec{r}_1, \vec{r}_2) \quad (1)$$

where H is the Hamiltonian operator given by

$$H = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{1}{r_1} - \frac{1}{r_2} + \frac{1}{|\vec{r}_1 - \vec{r}_2|} \quad (2)$$

and where Ψ is the system wavefunction. We then employ the basic idea of the close-coupling method which is to expand the total wavefunction Ψ in target states.^{2,5} We then obtain, in standard fashion of the close-coupling method, the following static exchange equation for the continuum orbital F

$$(\nabla^2 + k^2)F(\vec{r}) = U(\vec{r})F(\vec{r}) + (-1)^s \langle \hat{K} | F \rangle \quad (3)$$

where k is the projectile momentum, U is the static potential, and \hat{K} is the exchange kernel. The symbol s is 0 for singlet scattering and 1 for triplet scattering. F of Eq. (3) is required to satisfy the standard time-independent scattering boundary conditions⁵ of incoming plane waves and outgoing spherical waves.

We then expand the continuum orbital in partial waves according to

$$F(\vec{r}) = \sum_{l,m} f_l(r) Y_l^m(\theta, \phi). \quad (4)$$

We just keep the $l = 0$ term in Eq. (4); hence, we are considering only s-wave scattering. Thus the model is simple but realistic. Then, the partial s-wave continuum orbital f , satisfies the K-matrix boundary conditions given by

$$\lim_{r \rightarrow \infty} f(r) = A^{(K)} G^{(1)}(kr) + B^{(K)} G^{(2)}(kr) \quad (5)$$

where the K-matrix is given by

$$K = \tan(\delta) = B^{(K)}/A^{(K)}. \quad (6)$$

The T-matrix boundary conditions are given by

$$\lim_{r \rightarrow \infty} f(r) = A^{(T)} G^{(1)}(kr) + B^{(T)} H^{(+)}(kr) \quad (7)$$

where the T-matrix is given by

$$T = e^{i\delta} \sin(\delta) = B^{(T)}/A^{(T)}. \quad (8)$$

The $G^{(1)}$ and $G^{(2)}$ are related to the spherical Bessel functions by

$$G^{(1)}(kr) = kr j_0(kr) \quad (9)$$

and

$$G^{(2)}(kr) = -kr n_0(kr) \quad (10)$$

where j_0 is the $l = 0$ regular Bessel function and n_0 is the $l = 0$ irregular spherical Bessel function. Also, $H^{(+)}$ is the Hankel function of the first kind given by

$$H^{(+)}(kr) = G^{(1)}(kr) + iG^{(2)}(kr). \quad (11)$$

The static exchange differential equation for s-wave scattering is then changed into an integral equation, in standard fashion, which is called the Lippman-Schwinger equation, and is given by

$$f(r) = w^{(1)}(r) - (-1)^s \frac{1}{k} \int_0^\infty dy [w^{(1)}(r_<) w^{(2)}(r_>)]_{r,y} \int_0^\infty dx V^s(y,x) f(x) \quad (12)$$

where the w functions are related to the G s by

$$\begin{aligned} w^{(1)}(r) &= G^{(1)}(kr) \\ w^{(2)}(r) &= G^{(2)}(kr) + \beta G^{(1)}(kr) \end{aligned} \quad (13)$$

where $\beta = 0$ for the K-matrix case and $\beta = i$ for the T-matrix case. In Eq. (12), V^s is the sum of the static and exchange potential so that

$$V^s(y,x) = U(x)\delta(x-y) + (-1)^s \hat{K}(x,y) \quad (14)$$

Then, we have²

$$D = -\frac{1}{k} \langle w^{(1)} | V^s | f \rangle \quad (15)$$

where D is either the K- or T-matrix depending on the form of w^2 in Eqs. (12) and (13).

Then we expand f in a Slater basis set

$$\phi_n(\alpha, r) = r^{n-1} e^{-\alpha r} \quad (16)$$

according to

$$f(\alpha, r) = \sum_n C_n \phi_n(\alpha, r) \quad (17)$$

We then proceed in a standard fashion which may be taken from Ref. 6 or 7 or from many other places. We then obtain the following set of working equations:

$$D = -\frac{1}{k} \vec{C} \underline{M}^{-1} \vec{C} \quad (18)$$

where

$$C_m = \langle w^{(1)} | V^s | \phi_m \rangle \quad (19)$$

and

$$M_{mn} = \langle \phi_m | V^s - V^s \hat{G} V^s | \phi_n \rangle \quad (20)$$

In Eq. (21), \hat{G} is the reduced Green's function operator. Its form can be inferred by rewriting Eq. (12) in Dirac notation

$$|f\rangle = |w^{(1)}\rangle + \hat{G} V^s |f\rangle \quad (21)$$

and comparing Eq. (21) and (12).

Results and Conclusions

The \underline{M} of Eq. (18) can be written as

$$\underline{M} = \underline{M}_R + \beta \underline{M}_I \quad (22)$$

where $\beta = 0$ if we are using the K-matrix form and $\beta = i$ if we are using the T-matrix form. One of the surprising results of the present work is that \underline{M}_I is explicitly singular and cannot be inverted. This does not mean that \underline{M} is singular, since we can use the following results. If, in general,

$$\underline{M} \equiv \underline{A} + i\underline{B} \quad (23)$$

and

$$\underline{M}^{-1} \equiv \underline{C} + i\underline{D} \quad (23)$$

then

$$\underline{C} = [\underline{A} + \underline{B} \underline{A}^{-1} \underline{B}]^{-1} \quad (24)$$

and

$$\underline{D} = -\underline{C}\underline{B}\underline{A}^{-1} \quad (25)$$

However, if \underline{B} is singular, then, as the size of the matrices increases, the accuracy with which \underline{M}^{-1} can be computed decreases until the inverse is no longer accurate. In fact, for any matrix size, the inverse is somewhat corrupted. The accuracy of the inverse computation can be tested by constructing the unit matrix. Also, the results can be compared with the K-matrix result where there is no \underline{M}_J . The agreement between the phaseshifts decreases as the basis set size increases. On a 64 bit word length computer, however, the agreement was still eight significant figures for a 15x15 matrix. We would like to note that we attempted to alleviate this problem by using an orthogonalized basis set instead of the ϕ s of Eq. (16). This improved the agreement between the K-matrix and the T-matrix phaseshifts by one to two significant figures, but did not alleviate the problem. The conclusion to be drawn from these results seems to be that there is no point in using the T-matrix form if real basis functions are to be used.

Pseudo-resonances are encountered, just as in Ref. 2, for both the K-matrix and T-matrix forms. A surprising result, however, was that \underline{M}_R is not singular until the energy is very near the pseudo-resonance energy. You have to be right on top of the pseudo-resonance energy before you lose the ability to compute \underline{M}_R^{-1} . This is quite different from our experience with the Kohn anomalies.⁸ The explanation for this and for the existence of the pseudo-resonances can be understood by considering the argument given above in the Rationale for the supposed non-existence of the pseudo-resonances in the SVP. The finite rank potential that is substituted into the Lippman-Schwinger equation is given by

$$V^{sep} \approx V^s |\vec{\phi}\rangle \underline{\Delta} \langle \vec{\phi}| V^s \quad (26)$$

where

$$\underline{\Delta}^{-1} = \langle \vec{\phi} | V^s | \vec{\phi} \rangle \quad (27)$$

If V^s is energy independent (static potential), then V^{sep} is well behaved. If V^s is energy dependent, then there are going to be energies where $\underline{\Delta}$ does not exist. In other words, the phase shift that we are computing is indeed the exact phase shift for the separable potential V^{sep} . The problem is, the separable potential is non-physical at energies where $\underline{\Delta}$ does not exist.

We have now investigated the energy dependence of $\underline{\Delta}$ to see if the energies where pseudo-resonances occur are related in an identifiable way to the energies where the separable potential does not exist. The central result of this paper is the finding that they are exactly the same energies. Thus, we can predict the energy positions of the pseudo-resonances before we run the scattering calculation, and thus avoid the troublesome energies. This ability is aided by the fact that the pseudo-resonances are very narrow and become more narrow as the basis set size increases.

Acknowledgments

This work was supported by NASA Grant NCC 2-492 and by a grant of computer time from the Florida State University Supercomputer Computations Research Institute.

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